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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR-REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Contract No. N00014-86-K-0501

Synthesis and Characterization of Mixed Semiconductor-Transition  
Metal Clusters

Mark A. Johnson

Yale University  
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New Haven, Connecticut 06520

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Johnson, Mark A.

## PART I

### A. Papers Submitted to Refereed Journals (and not yet published).

1. "On the Origin of the Competition Between Photodetachment and Photofragmentation in the Hydrated Electron Clusters,  $(H_2O)_n^-$ " Lynmarie A. Posey, Paul J. Campagnola, Mark A. Johnson, Gang-Ho Lee, and Kit H. Bowen, *J. Chem. Phys.* June 1989 [NSF, ONR]
2. "A Pulsed, High Resolution Photofragmentation Spectrometer for Mass-Selected Cluster Ions," M. J. DeLuca and Mark A. Johnson, in preparation for *Rev. Sci. Instr.*
3. "A Simple Electron Acceleration/Deceleration Lens for Time-of-Flight Photoelectron Spectroscopy of Mass-Selected Negative Ions," C.-C. Han, Y.-F. Yen and M. A. Johnson, in preparation for *Rev. Sci. Instr.* June, 1989 [ONR]
4. "On the Photoabsorption of Negative Cluster Ions Near the Electron Detachment Threshold: A Study of the  $(O_2)_n^-$ ," Chau-Chung Han, Michael J. DeLuca, and Mark A. Johnson, in preparation for *J. Chem. Phys.*

### B. Papers Published in Refereed Journals

5. Michael J. DeLuca and Mark A. Johnson, "Photofragmentation of  $C_n^-$ ,  $4 \leq n \leq 20$ : Loss of  $C_3$ ," *Chem. Phys. Letters* 152, 67 (1988) [ONR, PYI].
6. Reactions of Hydrated Electron Clusters  $(H_2O)_n^-$ : Scavenging the Excess Electron," Lynmarie A. Posey, Michael J. DeLuca, Paul J. Campagnola and Mark A. Johnson, *J. Phys. Chem.* 93 [NSF]

### C. Book Sections Published

7. M. A. Johnson and W. C. Lineberger, "Pulsed Methods for Cluster Ion Spectroscopy," in *Techniques of Chemistry*, Vol. XX, *Techniques for the Study of Ion-Molecule Reactions*, Edited by J. M. Farrar and W. H. Saunders, John Wiley & Sons, 1988). P. 591.

### E. Technical Reports

8. "A Simple Electron Acceleration/Deceleration Lens for Time-of-flight photoelectron spectroscopy of mass-selected negative ions," C.-C. Han, Y.-F. Yen, and Mark A. Johnson, Report #6.
9. "A Pulsed, High Resolution Spectrometer for Mass Selected Ions," Michael J. DeLuca and Mark A. Johnson, Report #7.

10. "Wavelength Dependent Photofragmentation of Hydrated Electron Clusters,  $(H_2O)_n^-$ : A Half-Collision View of the Zero Energy Electron Capture Resonance," Paul J. Campagnola, Lynmarie A. Posey, Mark A. Johnson, Report #8 [NSF].

#### H. Invited Talks

11. "Electron transfer reactions of the hydrated electron clusters: Micro-calorimetry in a molecular beam," Dynamics of Molecular Collisions, Asilomar, CA. July 1989 [NSF].
12. "Cluster ions in reaction dynamics: Isolation and selective excitation of reaction intermediates," Spectroscopy of Free Radicals, Dalian, China, September, 1989 [NSF].
13. "Cluster analogues of the hydrated electron: Spectroscopy, Photochemistry and reactivity," Cluster symposium at Pacificchem '89, Hawaii, December, 1989 [NSF].
14. "Electron transfer reactions of the excess electron in  $(H_2O)_n^-$  clusters: molecular beam micro-calorimetry," Cluster symposium held at the ACS national meeting at Miami, Sept. 10-15, 1989.

#### I. Contributed Presentations at Topical or Scientific Conferences

15. "Photochemistry of Hydrated Electron Clusters,  $(H_2O)_n^-$  ( $15 \leq n \leq 40$ )," L.A. Posey and M. A. Johnson, Poster at the Fourth International Symposium on Small Particles and Inorganic Clusters, Aix-en-Provence, France, July, 1988.
16. "Photodissociation and Photodetachment of Hydrated Electron Clusters  $(H_2O)_n^-$ : The Mechanics of the Onset at  $n=15$ ," L. A. Posey and M. A. Johnson, Talk at the Fourth International Laser Science Conference, Atlanta, GA, October 1988.
17. "Pulsed Methods for Ion Spectroscopy," M. J. DeLuca and M. A. Johnson, poster at the Research Conference on Molecular Electronic Spectroscopy, Ile d'Oleron, France, September, 1988.
18. "Trapping of intermediate complexes in ion-molecule reactions: Photoelectron spectroscopy of three isomeric  $N_2O_2^-$  complexes," Lynmarie A. Posey and Mark A. Johnson, Poster at the Dynamics of Molecular collisions conference Asilomar, CA, July 1989.



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**J. Honors, Awards, and Prizes**

Presidential Young Investigator Award, 1987-1992  
National Science Foundation (Feb. 1987)

Junior Faculty Fellowship  
Yale University (1988-1989)

**K. Number of Graduate Students Receiving ONR Support**

None.

**L. Number of Post docs Receiving ONR Support**

One: 100%  
Dr. Chau-Chung Han  
Ph.D. Stanford University 1987

## PART II

Principal Investigator: Mark A. Johnson, Assistant Professor  
(203 432-5226)

ONR Scientific Officer: Dr. David L. Nelson (202-696-4409)

Project Description: Our primary objectives are to study the electronic and geometrical structures of mass selected cluster ions, with emphasis on clusters containing semiconductors, metals and mixed compositions. Our early efforts focussed on the use of ultraviolet photoelectron spectroscopy (UPS) of a mass selected negative ion beam to provide a low resolution diagnostic of the electronic band structure. In order to determine cluster geometries, we are expanding our techniques to include high resolution laser photofragmentation spectroscopy.

### Significant Results in the Past Year:

#### Technique development:

In the past year, we have completed construction of a single-longitudinal mode pulsed dye laser and demonstrated its performance on the mass-selected ion beam using  $\text{NNO}^+$  as a target ion. This system is state-of-the-art in terms of power and linewidth capabilities, which will be invaluable in unravelling the spectral congestion expected in the cluster systems. We have also been working on photoelectron spectroscopy on a technical level where we have developed a way to control the photon-energy resolution problem inherent in the pulsed PES technique which we developed at Yale.

#### Cluster Photophysics:

We have undertaken a series of experiments to understand why many cluster systems (e.g.  $\text{Ag}_n^-$ ,  $\text{C}_n^-$ ) efficiently photodissociate when excited near their electron detachment thresholds. We have looked at the water and oxygen negative ions, where water physically stabilizes the electron in an otherwise closed shell system while oxygen has an open shell structure similar to metal systems. The water experiment is particularly enlightening since we were able to show that the photodissociation propensity is simply related to the excess kinetic energy of the electron after excitation, which was determined using photoelectron spectroscopy. Thus, intra-cluster electron-phonon scattering appears to mediate the ability of clusters to capture the excited electron before it leaves the cluster.

#### Internal energy control:

In yet another "first," we have succeeded in controlling the internal energy content of  $(\text{H}_2\text{O})_n^-$  clusters by varying conditions of the expansion. So far we have seen cooling in the ensemble on the order of one monomer bond energy.

Summary of Plans for next year: Since our contract expires on July 1, 1989, we summarize likely future directions for this research. It is now clear that optical excitation of negatively charged clusters is quite complex and not understood even in very simple systems. A particularly fruitful direction therefore appears to be a high resolution study of the near threshold region of clusters in which the charge is initially localized. An outstanding candidate for this study is the  $I^-(O_2)_n$  clusters. Here, we envision two complementary experiments to probe the electron scattering after excitation where the photofragmentation cross section and the photoelectron spectra are obtained as a function of excitation energy near the  $I^-$  photodetachment threshold. A particularly exciting prospect is the opportunity to directly observe scattering into the autodetaching levels of  $O_2^-$  solvent molecules. This type of photon energy-dependent probe can then be extended to the case of metals which are characterized by a delocalized electron.

#### G. STUDENTS AND POSTDOCS

##### Students:

Lynmarie A. Posey  
Michael J. DeLuca  
Paul J. Campagnola  
Yu-Fong Yen  
Donna Cyr

##### Post-doc:

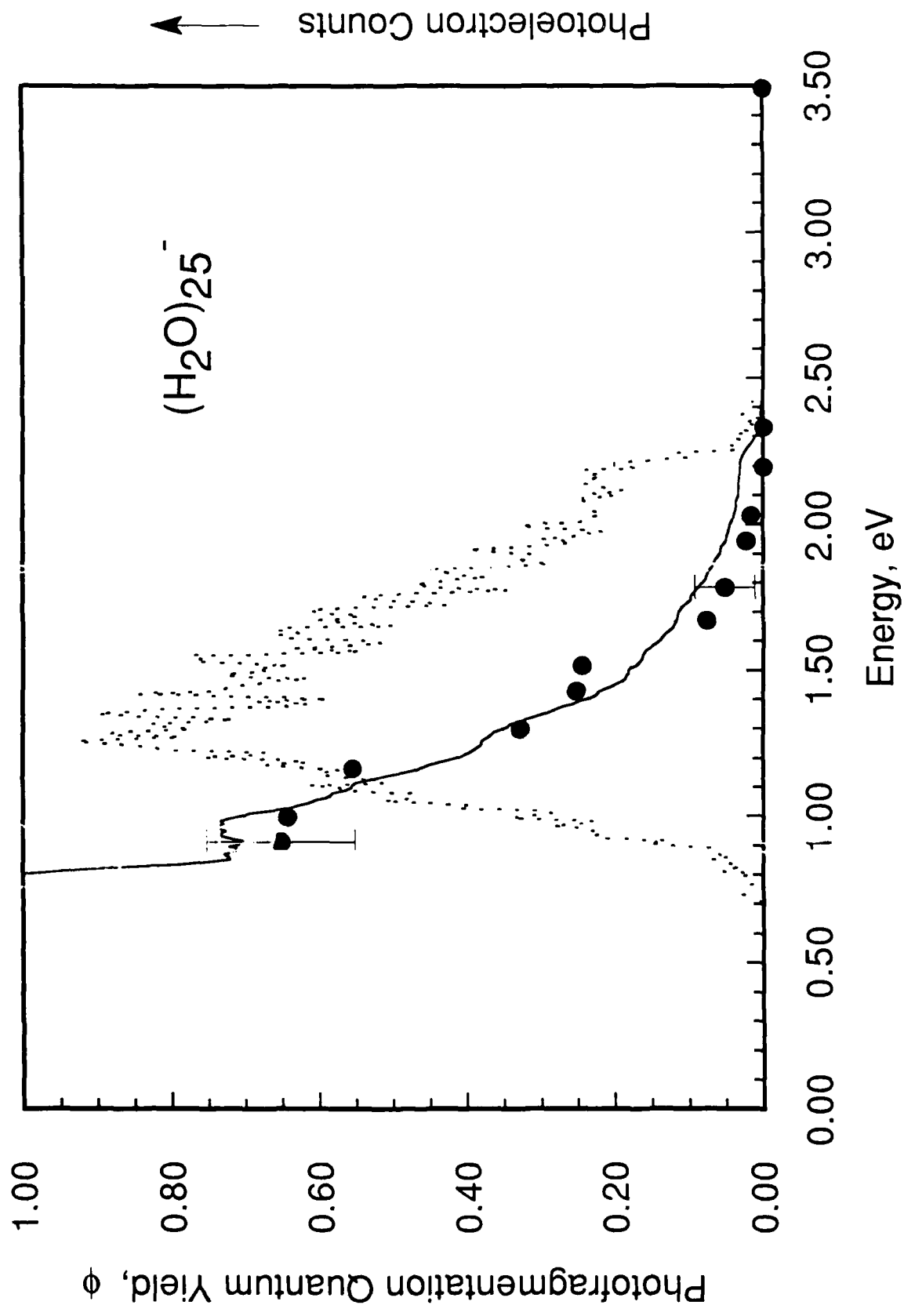
Dr. Chau-Chung Han

#### PART III.

SEE ATTACHED SHEETS

## **PROBING THE "CONDUCTION BAND" OF CLUSTERS WITH OPTICAL SPECTROSCOPY**

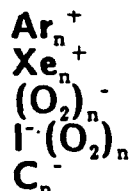
- 1. THE NEED FOR NEW DIAGNOSTICS**
- 2. DETERMINE THE ELECTRON BINDING ENERGIES USING  
PHOTOEMISSION-  
SIZE SELECTION USING  
NEGATIVE ION PHOTOELECTRON SPECTROSCOPY**
- 3. PHOTOEXCITE THE CLUSTER NEAR THE ELECTRON  
BINDING ENERGY**
- 4. MONITOR THE BRANCHING BETWEEN  
PHOTODETACHMENT AND PHOTOFRAGMENTATION**
- 5. LOOK FOR SIMPLE MODELS TO RECOVER BEHAVIOR OF  
BRANCHING RATIO USING ELECTRON-PHONON  
SCATTERING**





## CONCLUSIONS

1. PHOTOEXCITATION OF EXCESS ELECTRON IS  
CHANNELED INTO ELECTRON KINETIC ENERGY
2. CAPTURE OF THE ELECTRON IS MEDIATED BY  
INELASTIC SCATTERING SIMILAR TO THAT SEEN  
IN ELECTRON SCATTERING FROM SOLIDS
3. OTHER SYSTEMS STUDIED SO FAR WHICH INDICATE  
PHOTOEXCITATION OF THE ELECTRON OR HOLE  
INTO "CONDUCTING" STATES OF THE BULK:



4. RELEVANCE TO HETEROGENEOUS SYSTEMS:

EXPLORE CHARGE LOCALIZATION IN MIXED SYSTEMS  
SUCH AS  $[\text{O}_2\text{Ag}_n]^+$

#### PART IIID.

In the design of materials at the atomic and molecular level, we are lead to explore the properties of a collection containing anywhere from a few to a few hundred atoms, as these clusters may provide the building blocks for materials with tailored properties. A major challenge facing experimentalists studying these microscopic systems is that, while ordered solids can be characterized by many highly developed techniques (LEED, Auger, photoemission, conductivity, optical spectroscopy, etc.) the cluster systems require either entirely new or highly adapted methodologies to define their behavior.

We have therefore undertaken the task of developing cluster diagnostics and have succeeded in demonstrating a gas phase analogue of photoemission, negative ion photoelectron spectroscopy, on cluster systems. The novelty of this technique is that clusters with precisely determined compositions can be systematically studied as a function of size and stoichiometry. We are now working on methods for probing the nature of the conducting states in the clusters by photoexciting an excess electron and monitoring the propensity of the cluster to capture the outgoing electron before it escapes the clusters. This method couples photoelectron spectroscopy with photofragmentation spectroscopy to get the best overall view of the excited state dynamics.

In the figure shown in part IIIC., we show the photoelectron spectrum (dashed line) and photofragmentation quantum yield (points) of the excess electron attached to water clusters,  $(\text{H}_2\text{O})_{25}^-$ . The dashed line gives a map of the distribution of electron binding energies (taken by Kit Bowen at Johns Hopkins University), while the photofragmentation quantum yield provides a measure of the propensity of the photoexcited electron to escape. The solid line through the points is derived from a simple theory for the electron capture process where electrons photoexcited with less than 0.1 eV kinetic energy are captured with unity efficiency. Interestingly, this value of 0.1 eV is also the characteristic of the inelastic scattering of electrons off of solid water surfaces.

Future directions for this study include mixed metal/insulator systems such as oxygen adsorbed onto silver with an excess electron,  $[\text{O}_2\text{Ag}_n]^-$ . Here we investigate the propensity of the system to localize the charge on the  $\text{O}_2$  moiety and again look for excitation into the conduction band of the material, this time presumably into the states associated with the silver component of the clusters. Since the negative ion channel seems to mediate vibrationally inelastic scattering of CO from surfaces, this study can also provide a direct probe of the nature of the adsorbate in the presence of the negative charge.

OFFICE OF NAVAL RESEARCH  
CONTRACT #N00014-86-K-0501  
TECHNICAL REPORT #6

**A Simple Electron Acceleration/Deceleration Lens for Time-of-Flight  
Photoelectron Spectroscopy of Mass Selected Negative Ions**

C.-C. Han, Y.-F. Yen and M. A. Johnson

Department of Chemistry  
Yale University  
225 Prospect Street  
New Haven, CT 06511

In preparation for Publication

in

Review of Scientific Instruments

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## REPORT DOCUMENTATION PAGE

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4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #6		7a NAME OF MONITORING ORGANIZATION Chemistry Program	
6a NAME OF PERFORMING ORGANIZATION Yale University	6b OFFICE SYMBOL (if applicable)	7b ADDRESS (City, State and ZIP Code) 800 N. Quincy Street Arlington, VA 22217	
6c ADDRESS (City, State and ZIP Code) Department of Chemistry 225 Prospect Street New Haven, CT 06511	8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0501
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	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT NO.
11 TITLE (Include Security Classification) Characterization of Mixed Clusters			
12 PERSONAL AUTHOR(S) Mark A. Johnson			
13a TYPE OF REPORT Technical	13b TIME COVERED FROM _____ TO _____	14 DATE OF REPORT (Yr. Mo. Day) 88/7/25	15 PAGE COUNT
16 SUPPLEMENTARY NOTATION			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB GR	Cluster ion photoelectron spectroscopy, electron optics, PES of mass-selected clusters.
19 ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Since its introduction in 1986, pulsed photoelectron spectroscopy of mass selected ion beams is rapidly becoming a central tool in the study of cluster ions, molecular ions with high electron affinities (<math>\approx 3.5</math> eV) and even in the spectroscopy of the transition states of neutral chemical reactions. A traditional shortcoming of time-of-flight photoelectron spectroscopy when applied to negative ion beams is that the resolution, <math>\delta E</math> is highly dependent on the electron energy as:</p> $\delta E \propto E^{3/2} \times \Delta t$ <p>where <math>\Delta t</math> is the pulse width of the laser. We present a simple electrostatic lensing scheme which manipulates the electron kinetic energies in order to access the highest resolution possible to the spectral region of interest. An unanticipated benefit of this approach is that very low energy electrons can also be collected, allowing PES to probe the region very close to the electron binding energy.</p>			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b TELEPHONE NUMBER (include Area Code) 202-696-4410	22c OFFICE SYMBOL

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6c. ADDRESS (City, State and ZIP Code) Department of Chemistry 225 Prospect Street New Haven, CT 06511			7b. ADDRESS (City, State and ZIP Code) 800 N. Quincy Street Arlington, VA 22217	
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16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB GR	High resolution photofragmentation spectroscopy, pulsed tandem time-of-flight, techniques for cluster ion spectroscopy	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>We describe the performance of a pulsed spectrometer which creates ions using an ionized free jet, mass selects a particular m/e ion for interaction with a single-mode pulsed dye laser, and then analyzes the photofragments with a second mass spectrometer. Of particular interest is the result that the rotational cooling of the <math>N_2O^+</math> ion achieved in the source can be maintained even after extraction through the unskimmed jet. Details of the amplification scheme used in the frequency locked, single mode, pulsed dye laser are also presented.</p>				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
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OFFICE OF NAVAL RESEARCH  
CONTRACT #N00014-86-K-0501  
TECHNICAL REPORT #8

Wavelength Dependent Photofragmentation of Hydrated Electron  
Clusters,  $(\text{H}_2\text{O})_n^-$ : A "Half-Collision" View of the Zero Energy  
Electron Capture Resonance

L.A. Posey, Paul J. Campagnola, and Mark A. Johnson

Department of Chemistry  
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J.G. Eaton, G.H. Lee, and K.H. Bowen

Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218

Prepared for Publication  
in

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8c. ADDRESS (City, State and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0501		10. SOURCE OF FUNDING NOS.	
11. TITLE (Include Security Classification) Characterization of Mixed Clusters		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO.
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13c. SUPPLEMENTARY NOTATION		15. PAGE COUNT			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB GR	Threshold photofragmentation of negative cluster ions, electronic photophysics of cluster ions.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		
Photoexcitation of size-selected hydrated electron clusters, $(H_2O)_n^-$ , in the near IR results in a competition between photofragmentation and photodetachment. To investigate the origin of this competition, the decay probability into ionic fragments for the $n=25$ cluster was measured as a function of photon energy from 0.91 to 3.49 eV. The photofragmentation probability increases rapidly with decreasing excitation energy in the general vicinity of the vertical electron binding energy of this clusters (1.3 eV) determined via photoelectron spectroscopy. This result suggests that fragmentation accompanies photoexcitation of the excess electron with near zero kinetic energy. Thus, photofragmentation appears to proceed through an optically prepared intermediate similar to that reached in electron scattering from neutral clusters which displays an enhanced dissociative attachment pathway with near zero kinetic energy electrons.			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson			22b. TELEPHONE NUMBER (Include Area Code) 202-696-4410		22c. OFFICE SYMBOL

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FIELD	GROUP		
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) See attached sheet			
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OFFICE OF NAVAL RESEARCH  
CONTRACT #N00014-86-K-0501  
TECHNICAL REPORT #7

A Pulsed High Resolution Spectrometer for Mass Selected Ions

M. J. DeLuca and Mark A. Johnson

Department of Chemistry  
Yale University  
225 Prospect Street  
New Haven, CT 06511

In preparation for Publication

in

Review of Scientific Instruments

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In the design of materials, we are often faced with the problem that a desirable set of electrical or mechanical properties may be associated with a disordered or unstable stoichiometry of the system. The long standing problem of introducing Ohmic contacts onto GaAs is such an example where we seek a method of tailoring the junction with a partially diffused metal layer. We immediately ask the questions:

1. How do we determine the electronic properties of unstable, probably disordered systems?
2. How do these properties vary as the compositions are systematically varied?
3. How do we fabricate devices based upon these molecular-level building blocks?

In order to pursue the answers to these questions, we have initiated an avenue of research to explore the properties of atomic and molecular aggregates which are size selected using mass spectrometry and then analyzed using optical and photoelectron spectroscopies [technical report #1]. Thus, arbitrary compositions can be synthesized in a free jet expansion and interrogated directly in the gas phase. This methodology is sufficiently new that an entirely new class of species has only recently become amenable for study, creating a fertile ground for investigating the physical chemistry of heterogeneous systems at the atomic level [see technical reports #2 and #3].

The specific questions at the focus of our attention are the electronic structures and physical properties of cluster ions. In order to study the fundamental aspects of electrical conduction in these microscopic systems, we have chosen as a test case a system where only one electron is isolated in a sea of species which are polarizable but which have no available states

in which to propagate the electronic wavefunction. Such a system represents a kind of hydrogen atom for cluster research. The rare gas ions such as  $(\text{Xe})_n^-$  would appear ideal for such a study; however, they are exceedingly difficult to prepare. We, therefore, presently content ourselves with the  $(\text{H}_2\text{O})_n^-$  system as a prototype. We study this system using angle- and energy-resolved photoelectron spectroscopy, photofragmentation spectroscopy, and reaction chemistry [technical report #8]. We have, in fact, pioneered the development of a new technique, pulsed photoelectron spectroscopy of mass selected negative ions [technical report #1] to carry out this project.

Thus far in the water system we have determined the nature of the ground state electron configuration, the scattering events which occur upon photoexcitation and the competition between evaporation of the electron (deteachment) and a water monomer (fragmentation). We have extended these ideas to the carbon dioxide anion system, the rare gas cation systems  $(\text{Xe})_n^+$ ,  $(\text{Ar})_n^+$  with one extra hole instead of an electron, and finally, we begin to extend this work to systems to species with a high ground state degeneracy which characterizes metals and semiconductors where we have worked on oxygen [technical report #5] as well as on carbon  $\text{C}_n^-$  [technical report #4].

## Technical reports

1. "Demonstration of a pulsed photoelectron spectrometer on mass-selected negative ions:  $O^-$ ,  $O_2^-$ , and  $O_4^-$ ," L. A. Posey, Michael J. DeLuca and Mark A. Johnson.
2. "Pulsed photoelectron spectroscopy of negative cluster ions: isolation of distinguishable forms of  $N_2O_2^-$ ," L. A. Posey and M. A. Johnson.
3. "Photoelectron spectroscopy of  $(CO_2)_n^-$  clusters with  $2 < n < 13$ : cluster size dependence of the core molecular ion," M. J. DeLuca, B. Niu, and M. A. Johnson.
4. "Photofragmentation of  $C_n^-$ : loss of neutral  $C_3$ ," M. J. DeLuca and M. A. Johnson.
5. "Photofragmentation of  $(O_2)_n^-$ ,  $n=3,4$ : Direct determination of the  $O_2^-(v)$  vibrational distribution using pulsed photoelectron spectroscopy," C.-C. Han, Y.-F. Yen and M. A. Johnson.
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